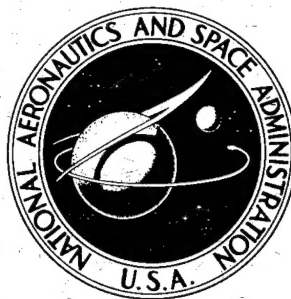


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OF THE PERFORMANCE
OF CHAR-FORMING ABLATORS

by Robert T. Swann

Langley Research Center

Langley Station, Hampton, Va.

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APPROXIMATE ANALYSIS OF THE PERFORMANCE OF CHAR-FORMING ABLATORS

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SUMMARY

Equations governing the performance of charring ablators, subject to a diffusion-controlled oxidation mechanism of char removal, are derived. A solution is presented for the case of a constant-enthalpy level. The effects of various material properties and environmental parameters are discussed.

INTRODUCTION

The charring plastics provide a practical method for protecting the interior of a reentry vehicle from the aerodynamic heating encountered during reentry. Much effort has been directed toward understanding the performance of these materials. Analytical models for charring ablators are presented in references 1 and 2. These references also present estimates of the weight of the charring ablator which is required to provide adequate thermal protection as a function of heating conditions and material properties. A more rigorous analytical model of the charring ablator is presented in reference 3. Results of some typical calculations are given in references 3 to 5.

A primary problem encountered in analyses of the performance of charring ablators is the removal of char from the surface. Aerodynamic shear, thermal stress, differential pressure, and oxidation have been suggested as mechanisms contributing to char removal. The removal of char as a result of pressure within the char, caused by confinement of the gaseous products of pyrolysis, is analyzed in reference 6. The effects of aerodynamic shear and thermal stress are not known in quantitative terms. Results of an extensive experimental investigation of the effects of oxidation on char removal and surface heating are presented in reference 7. In the test environment employed in the investigation (ref. 7), oxidation appeared to be the only mechanism involved in char removal. In the light of the results presented in reference 7, it appears that oxidation effects should be incorporated in the analysis of charring ablators.

The differential equation governing the performance of a charring ablator subject to a diffusion controlled mechanism of oxidation has been derived herein and is solved for a particular case. The effects of material properties and environmental factors on performance are discussed.

SYMBOLS

$$a = C_e \lambda N_{Le}^{0.6}$$

$$A = \frac{1 + \eta(a \Delta h + H_e - H_w)}{\Delta h_{eff}(1 + a\eta)}$$

C	concentration of oxygen
C _e	concentration of oxygen external to boundary layer
f	volatile fraction in uncharred material
Δh	heat of combustion per unit weight of char consumed
Δh _{eff}	effective heat of pyrolysis
Δh _p	heat of pyrolysis
H	total enthalpy
k	thermal conductivity
\dot{m}	rate of mass transfer
\dot{m}_c	rate of char removal
m _p	mass of gaseous products of pyrolysis
\dot{m}_p	rate of formation of gaseous products of pyrolysis
N _{Le}	Lewis number, N _{Pr} /N _{Sc}
N _{Pr}	Prandtl number
N _{Sc}	Schmidt number
q _l	heating of surface resulting from combustion
q _c	hot-wall convective heating rate
q _{c,o}	hot-wall convective heating rate with no mass transfer
q _r	radiant heating rate
Q	heat input

Q_c	total convective heat input
Q_r	total radiant heat input
t	time
T	absolute temperature
\bar{T}_s	average surface temperature during reentry
u	boundary-layer velocity parallel to surface
v	boundary-layer velocity normal to surface
W	thermal-protection weight per unit area (weight of material degraded)
W_c	char weight
x	boundary-layer coordinate parallel to surface
y	boundary-layer coordinate normal to surface

$$\beta = \frac{k_{ref} \rho}{\sigma \epsilon (T_{ref}^2 + T_p^2)(T_{ref} + T_p)}$$

δ_c	char thickness
ϵ	emissivity
η	transpiration factor
λ	weight of char removed per unit weight of oxygen diffusing to surface
μ	viscosity
ρ	char density
ρ'	density of boundary-layer fluid
σ	Stefan-Boltzmann constant

Subscripts:

e	external to boundary
i	initial value
m	extremum value
max	maximum value

O	value in absence of mass transfer
p	pyrolysis
r	radiant
ref	reference value
s	surface
w	at the wall

ANALYSIS

An analytical model of the charring ablator is presented in reference 1. This model is shown schematically in figure 1. The outer surface is subjected

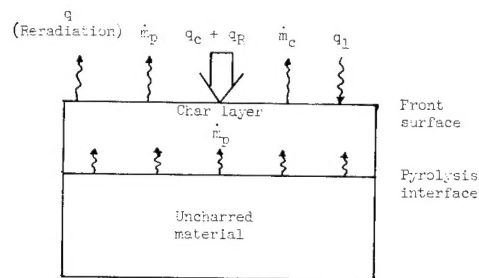


Figure 1.- Schematic diagram of charring ablator.

to aerodynamic heating. The char provides an insulating layer, and the heat passing through this layer is absorbed by pyrolysis at the interface between the char layer and the uncharred material. The surface of the char re-radiates a significant fraction of the heat input. The gases generated by pyrolysis transpire through the char layer and are injected into the boundary layer. The gases are heated as they pass through the char layer, and this removal of heat from the char layer reduces the quantity of heat conducted to the pyrolysis interface. When these gases are injected into

the boundary layer, the convective heat transfer to the surface is reduced. This reduction in convective heat as a result of mass injection is the same effect as that obtained with simple subliming ablators. In addition to the gases produced by pyrolysis, a residue remains at the interface and adds to the thickness of the char layer. This process tends to increase the thickness of the char layer. At the same time, char removal may occur as a result of thermal, chemical, or mechanical processes, and tends to decrease the thickness of the char layer.

The thermal behavior of charring ablators is very complex and, in general, numerical methods are required to solve the governing equations. However, if some simplifying assumptions are made, approximate expressions can be obtained for the char accumulation and the pyrolysis rate. Such approximate results are compared with the numerical results of reference 1, and the agreement is satisfactory. The effects of oxidation on char removal and heat input can be included in analyses similar to that of reference 1 without any particular difficulty. However, equations must be obtained for the rate at which oxidation removes char and the rate at which oxidation adds heat to the surface.

Oxidation

It is shown in reference 8 that the rate of oxidation of porous carbon in air is a diffusion controlled process, even at relatively low temperatures. Therefore, the rate of oxidation is controlled by the rate at which oxygen diffuses from the external stream to the surface. A detailed study of the removal of char by oxidation is presented in reference 7. In that study it is concluded that char removal occurs primarily as a result of oxidation. With sufficiently high surface temperatures (and hence high reaction rates), the oxygen diffusing to the surface reacts with the char rather than with the products of pyrolysis. The maximum rate at which oxygen diffuses to the surface is

$$\dot{m}(O_2) = \frac{q_c}{H_e - H_w} C_{eN_{Le}}^{0.6} \quad (1)$$

The derivation of equation (1) is outlined in the appendix.

If λ is the weight of char removed per unit weight of available oxygen, the rate of char removal is

$$\dot{m}_c = \frac{q_c}{H_e - H_w} C_{eN_{Le}}^{0.6} \lambda = a \frac{q_c}{H_e - H_w} \quad (2)$$

If Δh is the quantity of heat added to the surface per unit weight of char consumed, the rate at which the surface is heated by combustion is

$$\dot{q}_1 = \frac{q_c}{H_e - H_w} a \Delta h \quad (3)$$

The evaluation of λ and Δh is a complicated aero-thermal-chemical problem, the solution of which is beyond the scope of the present paper. However, limiting values can be indicated. The maximum value of λ is 0.75, which corresponds to the ratio of the molecular weights of carbon and oxygen when the product of oxidation is carbon monoxide. For this reaction, the value of Δh is approximately 4,000 Btu/lb. Carbon monoxide is the most probable product of a reaction occurring in an oxygen-deficient environment, and the formation of it is consistent with the results of reference 7.

The model of a charring ablator described previously is adequate for numerical analysis. With certain simplifications, the model can be reduced to a form for which analytical solutions can be obtained. First, it is assumed that the specific heat of the char layer is negligible. Solutions based on this assumption are compared with numerical solutions in reference 1 and the approximate solution provides an adequate representation of phenomena within the char, including char formation. A second assumption is that the effective conductivity of the char layer is a function of temperature as follows:

$$k = k_{\text{ref}} \frac{(T_s^2 + T_p^2)(T_s + T_p)}{(T_{\text{ref}}^2 + T_p^2)(T_{\text{ref}} + T_p)} \quad (4)$$

Because the specific heat of the char layer is negligible, the heat transferred across the char layer (from the surface to the reaction zone) is equal to $\frac{k(T_s - T_p)}{\delta_c}$. It is expected that the thermal conductivity of a porous material

such as a char layer will increase with increasing temperature because of the greater importance of radiation across the void spaces. The surface re-radiates energy at a rate proportional to its fourth power; therefore, relatively large changes in the heat input are required to obtain significant changes in the surface temperature. Therefore, by properly selecting the reference temperature T_{ref} , the error introduced by using equation (4) can be minimized. The actual error cannot be estimated because no data are presently available.

The model of a charring ablator presented in reference 1 can be readily extended to the case in which char removal and surface heating occur as a result of oxidation. The unknown quantities are the surface temperature, the rates of pyrolysis and char removal, the convective and combustive heating rates, and the weight of char accumulated. From these quantities, the weight of material degraded can be derived.

The approach which will be used is as follows. Energy balances at the heated surface and at the pyrolysis interface are used to eliminate the surface temperature. An approximate boundary-layer solution is used to express the convective heating rate in terms of the convective heating rate with no mass transfer and the mass-transfer rates. The char-removal rate and the combustive-heating rate are related to the convective-heating rate by equations (2) and (3). An equation for the weight of char accumulated is obtained by noting the combined effects of char formation and char removal. A differential equation relating the weight of char accumulated and the convective heat input with no mass transfer is then derived. This equation, together with the relation between char weight and amount of material pyrolyzed, is used to relate the weight of material degraded and the convective-heat input with no mass transfer.

A heat balance at the outer surface yields the following equation:

$$\begin{array}{ccccccc} q_c & + & q_l & + & q_r & = & \sigma \epsilon T_s^4 + \frac{k\rho}{W_c}(T_s - T_p) \\ \text{Convective} & & \text{Combustion} & & \text{Radiant} & & \text{Re-radiation} & & \text{Heat conducted} \\ \text{heating} & & \text{heating} & & \text{heating} & & & & \text{from surface} \end{array} \quad (5)$$

The heat conducted from the surface is absorbed by pyrolysis and by heating the gaseous products of pyrolysis to the surface temperature. The rate of pyrolysis is

$$\dot{m}_p = \frac{k\rho(T_s - T_p)}{W_c \Delta h_{eff}} \quad (6)$$

where

$$\Delta h_{eff} = \Delta h_p + \frac{C_p}{2}(\bar{T}_s - T_p) \quad (7)$$

is an effective heat of pyrolysis which includes the heat absorbed by the gases as they transpire through the char. Equation (7) is derived in reference 2. Equations (4), (5), and (6) can be combined to eliminate T

$$q_r + q_l + q_c = \dot{m}_p \Delta h_{eff} \left(\frac{W_c}{\beta} + 1 \right) \quad (8)$$

where

$$\beta = \frac{k_{ref}\rho}{\sigma\epsilon(T_{ref}^2 + T_p^2)(T_{ref} + T_p)}$$

and it is assumed that

$$T_p^4 \ll T_s^4$$

The convective-heating rate can be obtained from the relation

$$q_c = q_{c,o} \left[1 - \eta(\dot{m}_c + \dot{m}_p) \frac{H_e - H_w}{q_{c,o}} \right] \quad (9)$$

where $q_{c,o}$ is the hot-wall convective-heating rate with no mass transfer. Equation (9) is obtained by fitting a straight line to the boundary-layer solutions given in reference 9. It is valid only when the term

$$\eta(\dot{m}_c + \dot{m}_p) \frac{H_e - H_w}{q_{c,o}} < \frac{2}{3}$$

This condition is almost always satisfied when all the heat input is convective. A higher order approximation may be required if high radiant-heat inputs are also incident on the surface. It is assumed in equation (9) that the char which is oxidized and the pyrolysis products which are injected into the boundary layer are equally effective in blocking the convective heat input; this assumption explains the multiplication of \dot{m}_c and \dot{m}_p by the same value of η .

Actually, the blocking effectiveness depends on the molecular weight of the injected gases and probably differs for the products of combustion and pyrolysis. However, to the present order of approximation this difference may be neglected.

From equations (2) and (9), the rate of oxidation of the char is

$$\dot{m}_c = \frac{a}{1 + a\eta} \left(\frac{q_{c,o}}{H_e - H_w} - \eta \dot{m}_p \right) \quad (10)$$

and similarly the heat transfer to the surface (in terms of the heat transfer with no mass transfer and the rate of pyrolysis) is

$$q_c = \frac{(H_e - H_w) \dot{m}_c}{a} = \frac{q_{c,o} - \eta \dot{m}_p (H_e - H_w)}{1 + a\eta} \quad (11)$$

From equations (3) and (11), the rate at which the surface is heated as a result of combustion is

$$q_1 = \left(\frac{q_{c,o}}{H_e - H_w} - \eta \dot{m}_p \right) \frac{a \Delta h}{1 + a\eta} \quad (12)$$

To this point, a sufficient number of relations has been developed to express all the unknown variables in terms of the rate of pyrolysis, the weight of char accumulated, and the heating rate with no mass transfer. From consideration of the geometric effects of pyrolysis and char removal, the weight of char accumulated is related to the rates of pyrolysis and char removal as follows:

$$\frac{dW_c}{dt} = \frac{1 - f}{f} \dot{m}_p - \dot{m}_c \quad (13)$$

which states that the rate of change of char weight is equal to the difference between the rate at which char is formed and the rate at which char is removed. Equation (10) can be used to eliminate \dot{m}_c from equation (13). Thus,

$$\frac{dW_c}{dt} = \dot{m}_p \left[\frac{1 - f + a\eta}{f(1 + a\eta)} \right] - \frac{a q_{c,o}}{(1 + a\eta)(H_e - H_w)} \quad (14)$$

Equations (8), (11), (12), and (14) can be combined to yield the following equation:

$$\begin{aligned} & \frac{q_{c,o}}{H_e - H_w} \frac{a \Delta h + H_e - H_w}{\Delta h_{eff}(1 + a\eta)} + \frac{q_r}{\Delta h_{eff}} \\ &= \frac{f}{1 - f + a\eta} \left[(1 + a\eta) \frac{dW_c}{dt} + \frac{a q_{c,o}}{H_e - H_w} \right] \left[\frac{W_c}{\beta} + 1 + \eta \frac{(a \Delta h + H_e - H_w)}{\Delta h_{eff}(1 + a\eta)} \right] \quad (15) \end{aligned}$$

The quantities $q_{c,o}$, q_r , and $H_e - H_w$ are, in general, known functions of time. In an important special case to be discussed later, that is,

laboratory evaluation of charring ablators, W_c is a function of time whereas $q_{c,o}$, q_r , and $H_e - H_w$ are constants. Equation (15) is a nonlinear first-order ordinary differential equation which can be solved by numerical methods. When the weight of char has been determined, equation (14) can be integrated to determine the mass of the gaseous products formed by pyrolysis. The weight of material degraded to yield gaseous products and char is

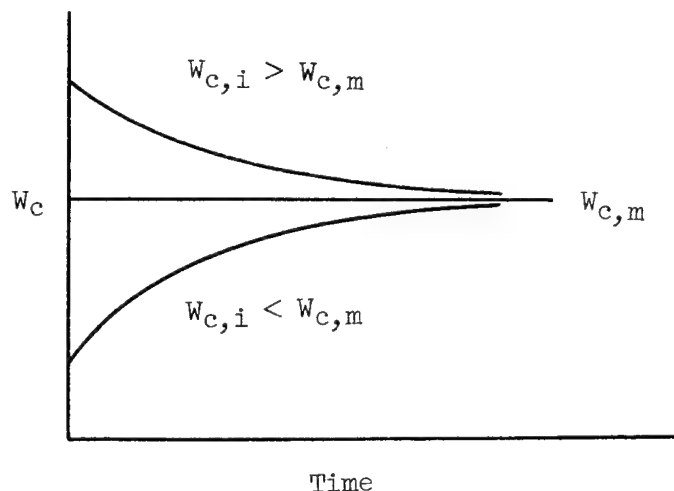
$$W = \frac{m_p}{f} + W_{c,i} \quad (16)$$

where $W_{c,i}$ is the char initial weight.

The equation governing the performance of a charring ablator (eq. (15)) cannot be integrated in general terms; however, certain significant information can be deduced from the equation without obtaining a solution. In addition, a solution can be obtained for a special case.

Extremum Char Weight

When the derivative of the char weight with respect to time vanishes, the char weight is an extremum. It will be seen later that the char weight is a monotonic function of heat input if other conditions are constant. Therefore, the extremum may be either a maximum or a minimum depending on whether the char weight is lesser or greater than the extremum char weight, as shown in sketch (a).



Sketch (a)

From equation (15), the extremum char weight is found to be

$$W_{c,m} = \beta \left[\left(\frac{\Delta h}{\Delta h_{eff}} + \frac{H_e - H_w}{a \Delta h_{eff}} \right) \frac{1 - f}{f} + \frac{q_r}{q_{c,o}} \frac{(H_e - H_w)}{\Delta h_{eff}} \frac{(1 - f + a\eta)}{af} - 1 \right] \quad (17)$$

It should be noted that, in general, $W_{c,m}$ is a function of time.

The extremum char weight is an important combination of material properties and environmental parameters, entirely aside from its interpretation as a limiting value. The extremum char weight depends on the heating only through the ratio of radiative to convective heating rates $q_r/q_{c,o}$, and it increases as the value of this ratio increases. The volatile fraction and the stream enthalpy

strongly influenced the extremum char weight, as shown in figures 2 and 3. The effects of oxygen concentration and radiant heating are discussed later.

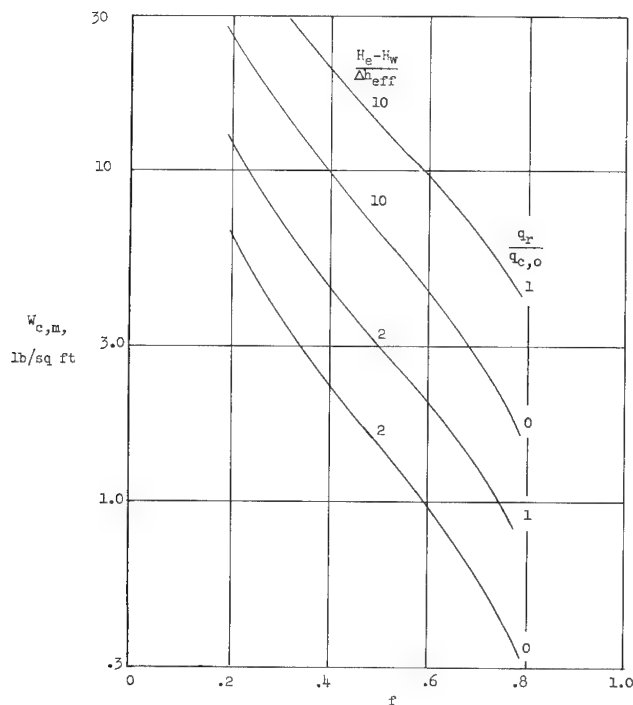


Figure 2.- Effect of volatile fraction on extremum char weight. $\lambda = 0.75$; $C_e = 0.20$; $\beta = 0.10$.

When the char weight approaches the extremum char weight, dW_c/dt approaches zero, from the definition of extremum char weight. When $\frac{dW_c}{dt} = 0$, the rate of pyrolysis is, from equation (14),

$$\dot{m}_p = \frac{a}{1 - f + a\eta} \frac{fq_{c,o}}{H_e - H_w} \quad (18)$$

For this condition, the rate of pyrolysis is independent of k , ρ , ϵ , and Δh_{eff} . The only material property affecting the pyrolysis rate is the volatile fraction f . This result can be understood when it is noted that, with $\frac{dW_c}{dt} = 0$, the rate at which char is formed (which is directly proportional to the rate of pyrolysis) is equal to the rate of char removal. However, the rate at which char is removed depends only on the rate at which oxygen diffuses to the surface. It should be noted that the time

required to approach the extremum char thickness increases as the extremum char thickness increases. The extremum char thickness is a function of the material properties as well as of the environmental conditions; therefore, the extent to which a given test will be influenced by the char weight approaching its extremum value is related to the properties of the material.

Caution must be exercised in the interpretation of test results when the char-formation characteristics in the test environment do not simulate those that exist in the flight environment. When the char thickness approaches its extremum value (for example, in low enthalpy tests), the response of the material is governed by relations which are quite different from those that apply in general. The only material characteristic which affects material performance under such conditions is the volatile fraction.

Solution for Constant Enthalpy

The most important single heating condition is that for which the stream enthalpy is constant and for this condition equation (15) can be integrated in

closed form, provided $q_r/q_{c,0}$ and C_e are constant. All of these conditions are typical of tests conducted in ground test facilities.

Equation (15) can be simplified to the following form by using equation (17):

$$\frac{dW_c}{dQ_c} = \frac{\frac{a}{1 + a\eta} \left(\frac{W_{c,m}}{\beta} - \frac{W_c}{\beta} \right) \frac{1}{H_e - H_w}}{\frac{W_c}{\beta} + 1 + \frac{\eta(a \Delta h + H_e - H_w)}{\Delta h_{eff}(1 + a\eta)}} \quad (19)$$

If the stream enthalpy is constant and any radiant heating is proportional to the convective heating, equation (19) is a linear first-order differential equation in Q_c with W_c as the independent variable. The solution of this equation is

$$\begin{aligned} \frac{W_{c,i} - W_c}{W_{c,m}} - \left(1 + \frac{A\beta}{W_{c,m}} \right) \log_e \frac{1 - \frac{W_c}{W_{c,m}}}{1 - \frac{W_{c,i}}{W_{c,m}}} \\ = \frac{a}{1 + a\eta} \frac{Q_c}{(H_e - H_w)W_{c,m}} \quad (20a) \end{aligned}$$

where

$$A = 1 + \frac{\eta(a \Delta h + H_e - H_w)}{\Delta h_{eff}(1 + a\eta)} \quad (20b)$$

The amount of pyrolysis that has occurred can be determined as a function of the heat input and the char thickness by integrating equation (14)

$$m_p = \frac{W_c - W_{c,i} + \frac{a}{1 + a\eta} \frac{Q_c}{H_e - H_w}}{\frac{1 - f + a\eta}{f(1 + a\eta)}} \quad (21)$$

The weight of material which has been thermally degraded (that is, pyrolyzed to yield gaseous products or char) is, from equations (16) and (21),

$$W = \frac{W_c - W_{c,i} + \frac{a}{1 + a\eta} \frac{Q_c}{H_e - H_w}}{\frac{1 - f + a\eta}{1 + a\eta}} + W_{c,i} \quad (22)$$

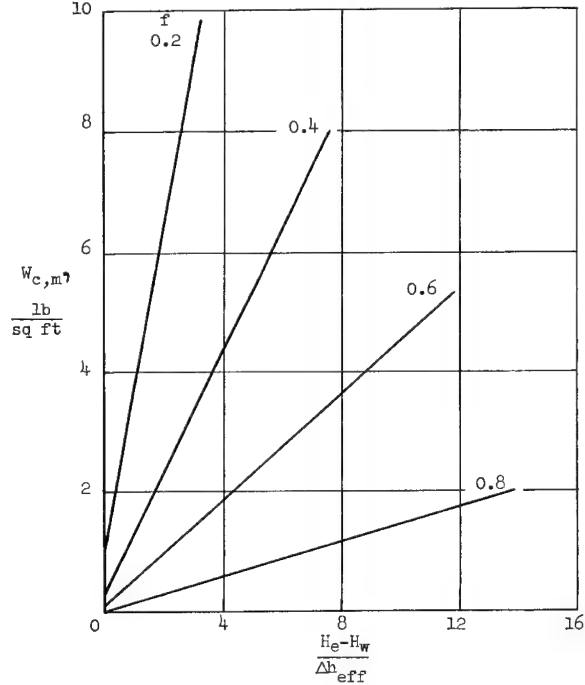


Figure 3.- Effect of enthalpy on extremum char weight. $q_r = 0$.

Because of the transcendental character of equation (20), the required weight of material cannot be expressed explicitly as a function of the heat input. However, equation (20) can be used to determine W_c as a function of Q_c . These results can be substituted into equation (22) to calculate the required weight.

Solution for No Char Removal

For the case in which no char removal occurs ($a = 0$), equation (15) has the following form:

$$\frac{f}{1-f} \frac{dW_c}{dt} \left[\frac{W_c}{\beta} + 1 + \frac{\eta(H_e - H_w)}{\Delta h_{eff}} \right] = \frac{q_{c,o} + q_r}{\Delta h_{eff}} \quad (23)$$

This form of the equation would apply to a material having characteristics similar to a charring ablator except that the surface does not oxidize and is not removed by mechanical forces. An impregnated ceramic shield might provide an example of this type of performance. This equation would also apply to reentry into a planetary atmosphere containing no oxygen or other chemical species which react with the char.

The solution of equation (23) is

$$\begin{aligned} \frac{W_c}{\beta} = & \left\{ \left[\frac{W_{c,i}}{\beta} + 1 + \frac{\eta(H_e - H_w)}{\Delta h_{eff}} \right]^2 + \frac{2(1-f)}{f} \frac{(Q_c + Q_r)}{\beta \Delta h_{eff}} \right\}^{1/2} \\ & - \left[\frac{W_{c,i}}{\beta} + 1 + \frac{\eta(H_e - H_w)}{\Delta h_{eff}} \right] \end{aligned} \quad (24a)$$

and the total weight of degraded material is

$$W = W_{c,i} + \frac{W_c}{1-f} \quad (24b)$$

If an average value of the enthalpy during reentry is assumed, this result is identical to that presented in reference 1.

DISCUSSION

Certain characteristic features of char formation and removal have been noted previously. In general, however, the equations governing the performance of charring ablators are too complex to yield significant information from a cursory examination. The effects of material properties and environmental parameters on system performance can best be evaluated on the basis of a parametric study. All the results presented in figures 4 to 9 are based on heating

in an airstream. Therefore, with a given heat input but with different enthalpies, the difference between the two results indicates the extent to which a test at one condition fails to simulate performance at the other condition; that is, it indicates the difference which results from failure to consider the variations in the two test conditions.

The relation between W/β and $\frac{Q}{\beta \Delta h_{eff}}$ is independent of the value of β . However, the required weight itself is not independent of β . For example, if β and Q both increase by a factor of 2, the required weight also increases by a factor of 2. Little information is available concerning the appropriate value of β . Based on a comparison of calculated results and a limited number of test results, the value of β for a 50-50 mixture of phenolic and nylon was found to be about 0.10.

Thermal-Protection Weight

The conditions for which equation (19) has been integrated are not representative of an actual spacecraft reentry. During such a reentry, the enthalpy decreases from its initial value to a negligible value; however, a significant fraction of the total heat input may be experienced before the decrease in enthalpy is appreciable. In tests conducted in ground facilities, a constant-enthalpy level is normally maintained and the present solution should be valid. Therefore, weights calculated from equations (20) and (22) are useful in evaluating the effects of environmental parameters and material properties on thermal-protection requirements and also in determining the significance of ground test results as they apply to a flight environment.

The thermal-protection weight (eq. (22)) is plotted as a function of the total heat input in figure 4. Although this weight does not include any allowance for insulation or for factors of safety, it will be referred to as the thermal-protection weight. The required weight is higher at the low enthalpy level than at the high enthalpy level for all values of total heat input. This condition results from the greater effect of oxidation and the lesser effect of blocking at the lower enthalpy.

Over the most important range of heat input, the optimum value of f is between 0.4 and 0.6, the lower value of f being associated with the higher heat input. However, for values of f between 0.4 and 0.6, the required weight is not extremely sensitive to the particular value that is used.

The effect of total heat input on required weight is shown in figure 5 for a value $f = 0.4$. With this linear total heat input scale, the decrease in the slope of the weight curve with increasing total heat input is readily observed. With no radiant heat input, the required weight is more strongly influenced by the enthalpy level. If one-half of the total heat input is radiant ($q_r/q_{c,0} = 1$), the required weight at a constant-enthalpy level is less than that for similar total heating in the absence of radiation. This effect is much more pronounced at the low-enthalpy level. Available test results, which are

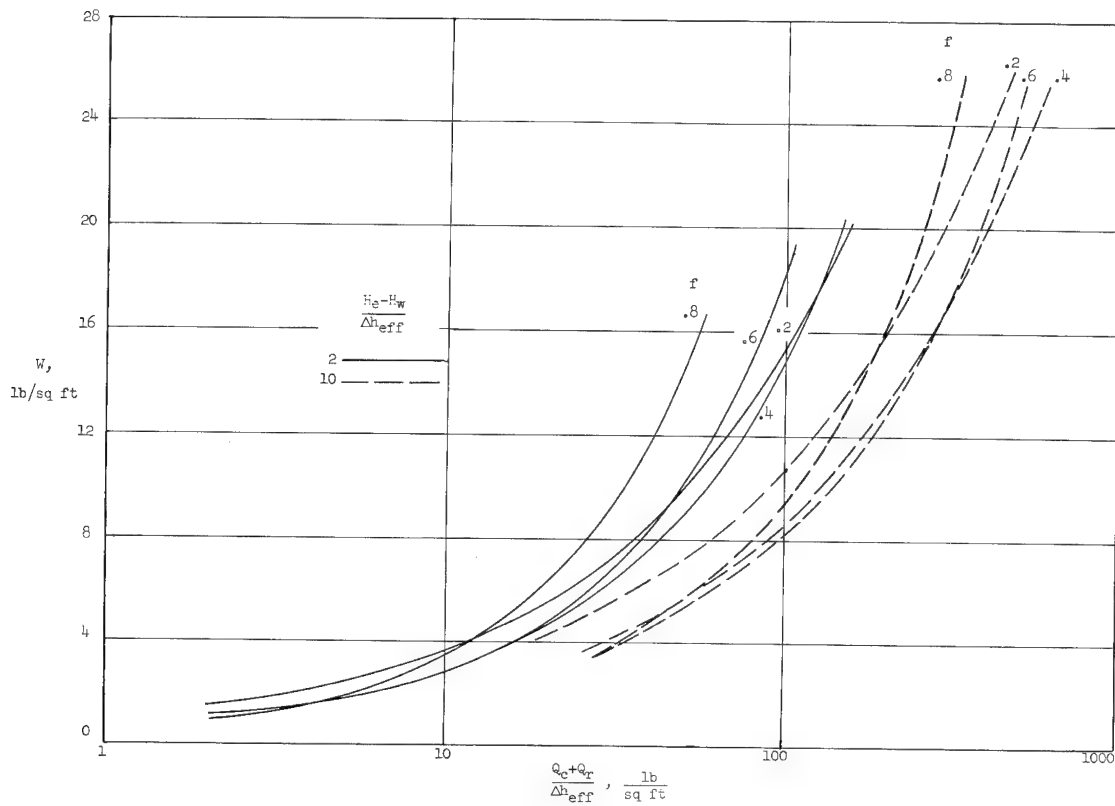


Figure 4.- Effect of heat input on required weight of ablating material.

reported on the basis of temperature rise rather than on the weight of material degraded, indicate that the effect of radiant heating on material performance is similar to an equal amount of convective heating.

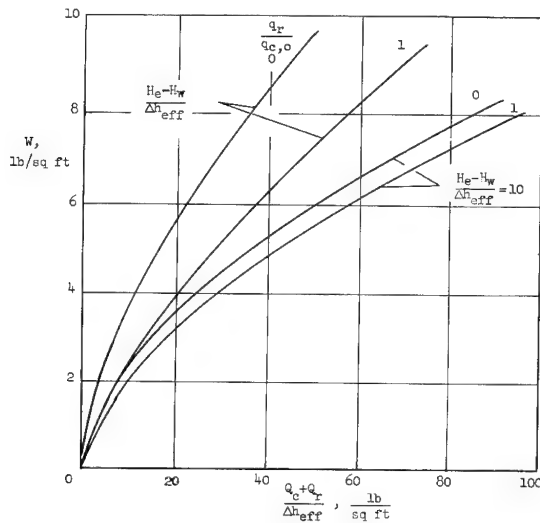


Figure 5.- Effect of total heating on required weight of ablating material. $f = 0.4$.

The effect of the enthalpy level on required weight is shown explicitly in figure 6 for selected values of total heat input. At the lower enthalpies, the required weight is very sensitive to the enthalpy value whereas at higher enthalpies the required weight is relatively insensitive to the enthalpy.

Thermal-Protection Effectiveness

It is difficult to define a simple parameter of considerable generality which provides a measure of the effectiveness of char-forming materials in the sense that the heat of ablation provides such a measure for subliming

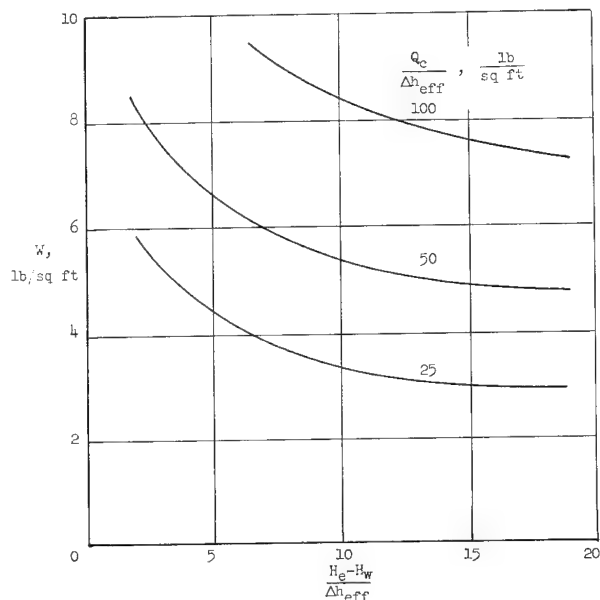


Figure 6.- Effect of enthalpy level on required weight of ablating material. $f = 0.4$; $q_r = 0$.

The effectiveness increases with increasing stream enthalpy and is greater for high total heat input than for lower heat input. The values shown in figure 7 are for a value of f of 0.4 which is less than the optimum value at high enthalpies. Therefore the estimated system effectiveness in figure 7 is less than the maximum theoretical value. At higher enthalpies the effectiveness of charring ablators is 8 to 14 times greater than the effective heat of pyrolysis for the range of important heat loads.

Accumulation of Char

The extremum char weight is a significant parameter in the performance of charring ablators; however, it is a limiting value and not necessarily a value that will be attained or even approached during a given heating cycle. For example, with a low volatile fraction and a high enthalpy level, extremum char weights in excess of 20 pounds per square foot (assuming $\beta = 0.10$) are predicted from figure 2. This value is greater than the estimated total thermal

ablators. A parameter consisting of a total heat input divided by the thermal-protection weight required to accommodate this heat input, which has been used in a number of investigations, appears to provide the best available characterization of charring ablators:

$$E = \frac{Q_c}{W} + Q_r$$

The weight in this equation is that required to assure the back surface of a shield subjected to the total heat input $Q_c + Q_r$ will not exceed the temperature of pyrolysis. Some results of the present study are presented in terms of the ratio of this parameter to Δh_{eff} in figure 7.

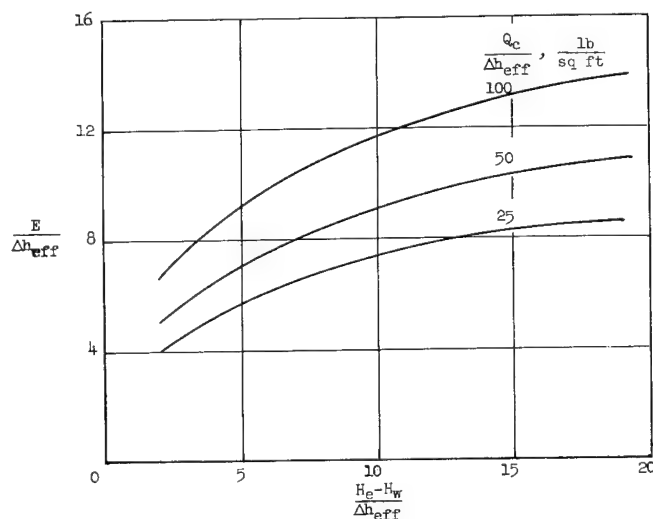
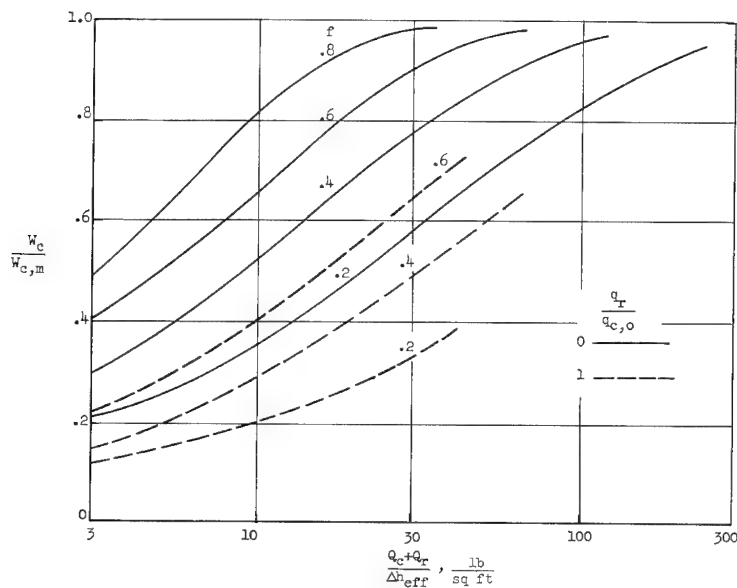


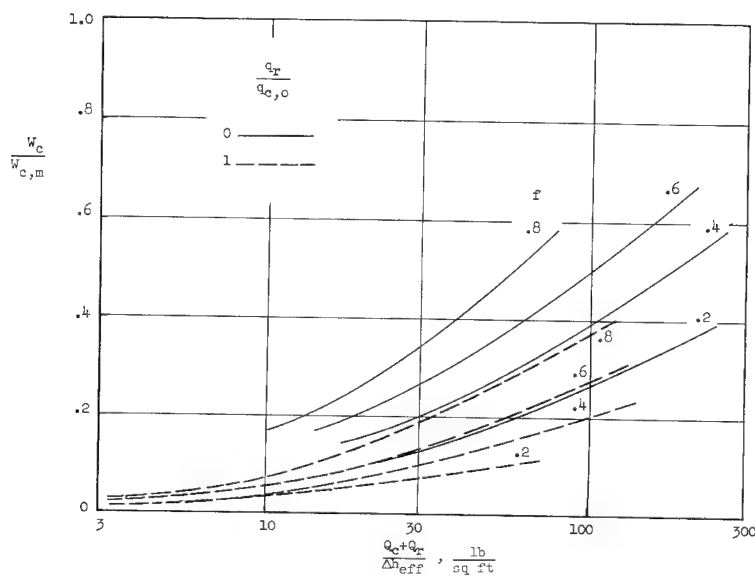
Figure 7.- Effect of enthalpy level on effectiveness of ablating material. $f = 0.4$; $q_r = 0$.

protection weight requirements for the stagnation point of a vehicle entering the earth's atmosphere at hyperbolic velocity. (See ref. 4.) Therefore, it is necessary to examine actual char weights in relation to extremum char weight

as a function of the total heat input. The char weight as a fraction of the extremum char weight is plotted in figure 8 as a function of total heat input, with zero initial char weight.



(a) Low enthalpy. $\frac{H_e - H_w}{\Delta h_{eff}} = 2.$



(b) High enthalpy. $\frac{H_e - H_w}{\Delta h_{eff}} = 10.$

Figure 8.- Effect of heat input on the relative magnitudes of char weight and extremum char weight.

At the lower enthalpy level (fig. 8(a)), W_c approaches $W_{c,max}$ at relatively low total heat inputs, particularly when the volatile fraction is high. At the higher enthalpy level (fig. 8(b)), the char thickness is considerably less than its maximum value, even with high total heat inputs and a high volatile fraction. Therefore, at low enthalpy levels the performance of a charring ablator is strongly influenced by the char thickness approaching its maximum value, whereas at high enthalpy levels, the approach of the char weight to a maximum value is barely evident. When radiant heating is present, the char weight as a fraction of its maximum value is greatly reduced for given total heat input.

That $W_c/W_{c,max}$ is a dominant factor in the performance of charring ablators is evident from the basic equation (eq. (20)). The total heat input required to produce a char weight (with $W_{c,i} = 0$), that is, within $1/e$ of the maximum char weight is plotted in figure 9 as a function of f . An increase in the enthalpy

level by a factor of 5 results in an increase by a factor of 20 in the heat input required to achieve the given value of $W_c/W_{c,max}$.

LIMITATIONS AND EXTENSIONS OF ANALYSIS

The method of analysis presented herein is based on a diffusion controlled oxidation of the char surface. This mechanism has been verified in a series of tests of 50-percent-phenolic-50-percent-nylon specimens. These tests were conducted in an atmospheric-pressure arc-heated jet with a heating rate of about 180 Btu/ft²-sec. For tests of other materials or for tests in a different environment, other mechanisms of char removal may be important. Even when oxidation is the only mechanism involved in char removal, the process will be reaction-rate controlled rather than diffusion controlled when the heating rates, and conse-

quently the surface temperatures, are sufficiently low. If mechanical forces such as shear stresses, differential pressures, or thermal stresses are a factor in char removal, these effects must be superposed on the effects of oxidation.

In the present analysis it has been assumed that pyrolysis occurs at the desired back surface temperature and therefore no additional insulation or cooling is required. Since this condition is not usually satisfied with actual materials, the analysis can be used only to calculate the amount of material that will be pyrolyzed. The effect of the heat conducted from the pyrolysis zone into the uncharred material on the rate of pyrolysis can be accounted for by adjusting the heat of pyrolysis to include the heat required to raise the material from its initial temperature to the pyrolysis temperature. The actual temperature response of the uncharred material and of the structure must be determined on the basis of a separate analysis.

In deriving the basic differential equation, no assumptions have been made regarding the functional dependence of the enthalpy or of the radiant heating; therefore, if these parameters are expressed as functions of Q_c , equation (19) is still a valid relation, and solutions can be obtained by numerical methods.

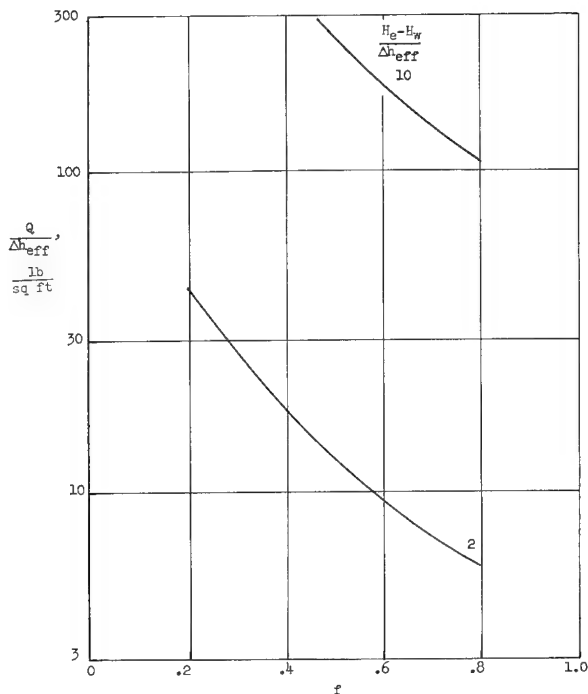


Figure 9.- Heat input required for char weight to reach $1/e$ of extremum char weight.

$$\frac{W_c}{W_{c,m}} = 1 - \frac{1}{e}; \quad q_r = 0.$$

In particular, if the enthalpy and radiant heating are slowly varying functions of Q_c , a solution can be obtained by successive applications of equations (20a) and (22); that is, the final value of W_c in each calculation becomes the initial value in the succeeding calculation. The appropriate current values of all the environmental parameters must be used in each step of the calculation.

CONCLUDING REMARKS

A diffusion-controlled oxidation mechanism for the removal of char at the surface of a char-forming material can be incorporated in an approximate analysis, and the performance of such materials in various thermal environments can be evaluated. For a given material and environment, there exists an extremum char weight. The performance of a material at any time is a function of the ratio of the actual char weight to the extremum char weight.

When the actual char weight approaches the extremum char weight, the rate of pyrolysis approaches a limiting value which is independent of the thermal conductivity and surface emissivity of the char and of the heat of pyrolysis. The extremum char weight increases linearly with the enthalpy level; therefore, the actual char weight approaches the extremum value much more quickly in tests conducted at low-enthalpy levels than in a high-enthalpy reentry environment. This factor must be considered in evaluating the significance of results obtained in facilities which provide a low-enthalpy test stream.

The effects of radiant heating on the performance of charring ablators appear in the governing equations only in the extremum char thickness relation. The analysis indicates that with constant total heat input the effectiveness of such materials increases with the substitution of a small component of radiant heating for convective heating. This increase in effectiveness is much more pronounced at low enthalpies than at high enthalpies.

Langley Research Center,
National Aeronautics and Space Administration,
Langley Station, Hampton, Va., December 3, 1963.

APPENDIX

ANALYSIS OF OXIDATION

The oxidation of carbon surfaces in hot airstreams has been extensively studied analytically. (See refs. 5 to 7.) It is found that at low surface temperatures the rate of oxidation of carbon is controlled by the reaction rates. At higher surface temperatures, however, the process is diffusion controlled; that is, the rate of oxidation is limited by the quantity of oxygen diffusing to the surface through the boundary layer. For porous carbon surfaces, the temperature at which the process becomes diffusion controlled is lower than it is for nonporous surfaces.

The char layer that is formed when charring ablators are heated tends to be porous, as evidenced by the fact that the gaseous products of pyrolysis transpire through it. In addition, injection of these pyrolysis products into the boundary layer reduces the quantity of oxygen diffusing to the surface. It is anticipated, therefore, that the oxidation of the char surface will be diffusion controlled, even at relatively low temperatures.

The rate at which oxygen diffuses to the surface is determined from the boundary-layer equation for conservation of oxygen. This equation is (ref. 8)

$$\rho'u \frac{\partial C}{\partial x} + \rho'v \frac{\partial C}{\partial y} = \frac{\partial}{\partial y} \left(\frac{\mu}{N_{Sc}} \frac{\partial C}{\partial y} \right) \quad (A1)$$

The energy equation can be expressed in the following form:

$$\rho'u \frac{\partial H}{\partial x} + \rho'v \frac{\partial H}{\partial y} = \frac{\partial}{\partial y} \left[\frac{\mu}{N_{Pr}} \frac{\partial H}{\partial y} + \frac{\mu}{2} \left(1 - \frac{1}{N_{Pr}} \right) \frac{\partial u^2}{\partial y} \right] \quad (A2)$$

Equations (A1) and (A2) are based on a nonreacting mixture of two gases having the same heat capacity. If $N_{Pr} = 1$ or if $\partial u^2 / \partial y$ is small compared with $\partial H / \partial y$, which is valid at stagnation regions, equation (A2) may be expressed approximately as follows:

$$\rho'u \frac{\partial H}{\partial x} + \rho'v \frac{\partial H}{\partial y} = \frac{\partial}{\partial y} \left(\frac{\mu}{N_{Pr}} \frac{\partial H}{\partial y} \right) \quad (A3)$$

The maximum rate of diffusion of oxygen to the surface is obtained when the concentration of oxygen at the wall vanishes. The boundary conditions on equations (A1) and (A3) are

$$\left. \begin{aligned} C &= 0 \\ H &= H_w \end{aligned} \right\} \begin{aligned} (y = 0) \\ (y = 0) \end{aligned} \quad (A4)$$

$$\left. \begin{aligned} C &\rightarrow C_e \\ H &\rightarrow H_e \end{aligned} \right\} \begin{aligned} (y = \infty) \\ (y = \infty) \end{aligned} \quad (A5)$$

The oxygen concentration and the enthalpy can be replaced by the dimensionless variables:

$$\bar{C} = \frac{C}{C_e} \quad (A6a)$$

$$\bar{H} = \frac{H - H_w}{H_e - H_w} \quad (A6b)$$

In terms of these new variables, equations (A1), (A3), (A4), and (A5) are

$$\rho' u \frac{\partial \bar{C}}{\partial x} + \rho' v \frac{\partial \bar{C}}{\partial y} = \frac{\partial}{\partial y} \left(\frac{\mu}{N_{Sc}} \frac{\partial \bar{C}}{\partial y} \right) \quad (A7a)$$

$$\rho' u \frac{\partial \bar{H}}{\partial x} + \rho' v \frac{\partial \bar{H}}{\partial y} = \frac{\partial}{\partial y} \left(\frac{\mu}{N_{Pr}} \frac{\partial \bar{H}}{\partial y} \right) \quad (A7b)$$

$$\bar{C} = \bar{H} = 0 \quad (y = 0) \quad (A7c)$$

$$\bar{C} = \bar{H} \rightarrow 1 \quad (y = \infty) \quad (A7d)$$

Because of the formal similarity of equations (A7a) and (A7b) and their boundary conditions (A7c) and (A7d), if the solution of equation (A7b) is

$$\bar{H} = \varphi(x, y, N_{Pr}) \quad (A8a)$$

the solution of equation (A7a) is

$$\bar{C} = \varphi(x, y, N_{Sc}) \quad (A8b)$$

where φ is the same function in both cases. It is shown in reference 10 that $\varphi(x, y, N_{Pr})$ can be expressed as

$$\varphi(x, y, N_{Pr}) = N_{Pr}^{0.4} \varphi_1(x, y) \quad (A8c)$$

Therefore,

$$\varphi(x, y, N_{Sc}) = N_{Sc}^{0.4} \varphi_1(x, y) \quad (A8d)$$

The rate at which oxygen diffuses to the wall is

$$\dot{m}(O_2) = C_e \left(\frac{\mu}{N_{Sc}} \frac{\partial \bar{C}}{\partial y} \right)_w \quad (A9a)$$

The aerodynamic heating rate is

$$q_c = (H_e - H_w) \left(\frac{\mu}{N_{Pr}} \frac{\partial \bar{H}}{\partial y} \right)_w \quad (A9b)$$

The ratio of rate of diffusion of oxygen to the surface to the heat-transfer rate is

$$\frac{\dot{m}(O_2)}{q_c} = \frac{C_e}{H_e - H_w} \frac{\left(\frac{\mu}{N_{Sc}} \frac{\partial \bar{C}}{\partial y} \right)_w}{\left(\frac{\mu}{N_{Pr}} \frac{\partial \bar{H}}{\partial y} \right)_w} = \frac{C_e}{H_e - H_w} \frac{\left[\mu N_{Sc}^{-0.6} \frac{\partial \phi_1(x,y)}{\partial y} \right]_w}{\left[\mu N_{Pr}^{-0.6} \frac{\partial \phi_1(x,y)}{\partial y} \right]_w} = \frac{C_e}{H_e - H_w} N_{Le}^{0.6} \quad (A9c)$$

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<p>NASA TR R-195 National Aeronautics and Space Administration. APPROXIMATE ANALYSIS OF THE PERFORMANCE OF CHAR-FORMING ABLATORS. Robert T. Swann. June 1964. 22p. OTS price, \$0.75. (NASA TECHNICAL REPORT R-195)</p> <p>Equations governing the performance of charring ablators, subject to a diffusion-controlled oxidation mechanism of char removal, are derived. A solu- tion is presented for the case of a constant-enthalpy level. The effects of various material properties and environmental parameters are discussed.</p>	<p>I. Swann, Robert T. II. NASA TR R-195</p>	<p>NASA</p>
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